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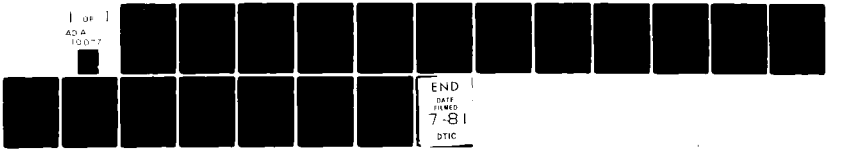

AN EXPERIMENTAL INVESTIGATION OF THE MELTING BEHAVIOR OF SMALL METAL PARTICLES

FINAL REPORT

by

W. A. Jesser

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U. S. ARMY RESEARCH OFFICE

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A dark-field transmission electron microscope technique was applied to a collection of submicron sized metal crystallites prepared by in-situ physical vapor deposition onto an amorphous carbon substrate in a vacuum of 2 x 10^{-7} torr in order to determine the melting behavior of individual crystallites. It was found that each particle melted suddenly at a single temperature which decreased with decreasing size. No liquid sheath was observed at any time. The melting temperature seemed to

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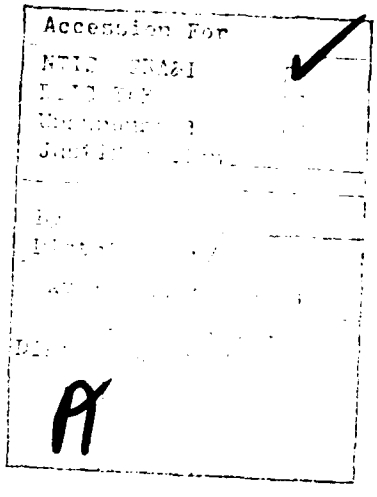
decrease nearly linearly with increasing surface curvature. Flat platelets with a near zero surface curvature but a significant surface to volume ratio showed no noticible size dependence of melting temperature. Oxidation of the particles raised their melting temperature as did embedding the particles in an amorphous carbon matrix. A simple thermodynamic model can account for all of the above observed effects.



FORWARD

The research work here is largely experimental and required a lengthy construction time for equipment. The specimen area of the Departmental Siemens Elmiskop 1A electron microscope was replaced by a differentially pumped ultra high vacuum chamber capable of in-situ deposition of fine particles whose individual melting temperatures can be measured. The characterization of the melting behavior of unalloyed metal particles was determined as a function of particle shape, size, and degree of oxidation. The effect of embedding particles in an inert matrix was also determined. These results were interpreted by developing a thermodynamic model.

The research work presented here is viewed as a coherent body of knowledge acquired in one laboratory through the use of one technique. Because of this uniformity of technique, one has eliminated the uncertainty which arises during a comparison of data from different laboratories in which diverse experimental approaches have been employed. The application of a single approach to the study of several materials and the effects of several variables allows one to construct more meaningful conclusions about the melting behavior of finely dispersed metal particles.

STATEMENT OF THE PROBLEM STUDIED

There are a number of processes which rely on the high temperature performance and characteristics of small particles. Among the important ones are sintering, powder metallurgy, catalysts, and rapid solidification processing. The melting behavior of finely dispersed particles is important to all of these areas of research as well as being of fundamental interest.

In order to understand the melting mechanisms, several important questions were raised and answered to various extents by the research sponsored by ARO from June 1, 1977 through December 31, 1980. The goals of the investigation were to determine:

1. whether the size-dependent melting of an individual particle occurs at a fixed temperature or over a temperature range.
2. whether melting of small particles proceeds by a thickening of a surface layer of liquid as the temperature of the particle is increased.
3. the relative slopes of the reduced temperature versus inverse radius plots for various metals.
4. the influence of particle shape and its concomitant surface to volume ratio on melting temperature.
5. the influence of oxidation on the melting behavior.
6. whether there are limiting sizes or temperatures to the size-dependent melting temperature.
7. how the melting of an isolated particle differs from that of a nearly continuous film.
8. the effect of embedding isolated particles in an inert matrix.

9. whether a thermodynamic model can account for the observed behavior.

In order to conduct an investigation into the melting behavior of small particles, an ultra high vacuum chamber was constructed for use on a Siemens 1A transmission electron microscope. The particles were prepared in this chamber by physical vapor deposition onto an amorphous carbon substrate. The individual microcrystals whose diameters ranged between 3nm and 300nm were heated in a radiation cavity of known temperature and observed by dark-field electron microscopy. Sequences of dark-field micrographs with increasing temperature for a given specimen area provide the data necessary to achieve the goals of the research. The metals studied include tin, lead, indium and bismuth, with preliminary results from aluminum being inconclusive, and hence omitted from this report.

SUMMARY OF THE MOST IMPORTANT RESULTS

The following conclusions may be drawn from the results obtained by studying the melting behavior of tin, bismuth, indium and lead by a common dark-field transmission electron microscopy technique applied to individual microcrystals prepared by in-situ physical vapor deposition onto an amorphous carbon substrate in a vacuum of 2×10^{-7} torr. These results were obtained by the students mentioned in the personnel section.

1. The melting temperature of individual microcrystals was not found to occur over a temperature range, but rather each particle suddenly melted at a single temperature.
2. Observations failed to reveal the presence of a liqud sheath surrounding a solid core. The resolution of the technique is near 1nm and hence a liquid sheath of that thickness or less could be present yet undetected. This result negates the model of a slowly thickening liquid sheath with increasing temperature. It is consistent with the sudden and rapid propagation of a solid-liquid interface across a particle.
3. The melting temperature T_m of isolated microcrystals depends on size and shape, i.e. surface curvature, in a regular way with a nearly linear relationship being found between T_m and inverse radius for the diameter range 20nm and greater. The results for the four metals studied are plotted in figure 1 as reduced temperature T_m/T_o where T_o is the bulk melting temperature. The lines are least squares fit to the data and have slopes for T_m/T_o versus inverse particle radius of -0.903nm (freshly deposited tin), -0.317nm (previously melted

tin), -0.667nm (bismuth), -0.552nm (indium), -0.557nm (lead).

4. Melting temperature data obtained from flat platelets show that they do not exhibit a size dependent melting temperature over a range of surface to volume ratio which changes by a factor of 3. Particles whose shape was nearly spherical, with the same surface to volume ratio as the platelets, exhibited a size dependent melting temperature. All of the data on this shape effect lie near the bulk melting temperature where precision becomes important, and hence it should be confirmed over a wider range of platelet sizes. The data suggest that surface curvature is more important than surface to volume ratio in determining the size dependent melting temperature. The practical value tentatively suggested by this result is that platelet particles appear to melt at higher temperatures than equiaxed microcrystals. Powders in the form of platelets with a high surface to volume ratio may have good high temperature stability as compared to that for equivalent surface to volume ratio equiaxed microcrystals.

5. The effect of oxidation on the melting point of isolated microcrystals has been directly studied for the case of tin microcrystals. Purposeful oxidation of the liquid particle shows that melting of the oxidized solid occurs at a higher temperature than the unoxidized solid. The data of figure 1 for previously melted tin particles primarily shows this effect of oxidation. In this case the oxide which formed was SnO rather than the Sn_3O_4 or SnO_2 found in bulk systems at the

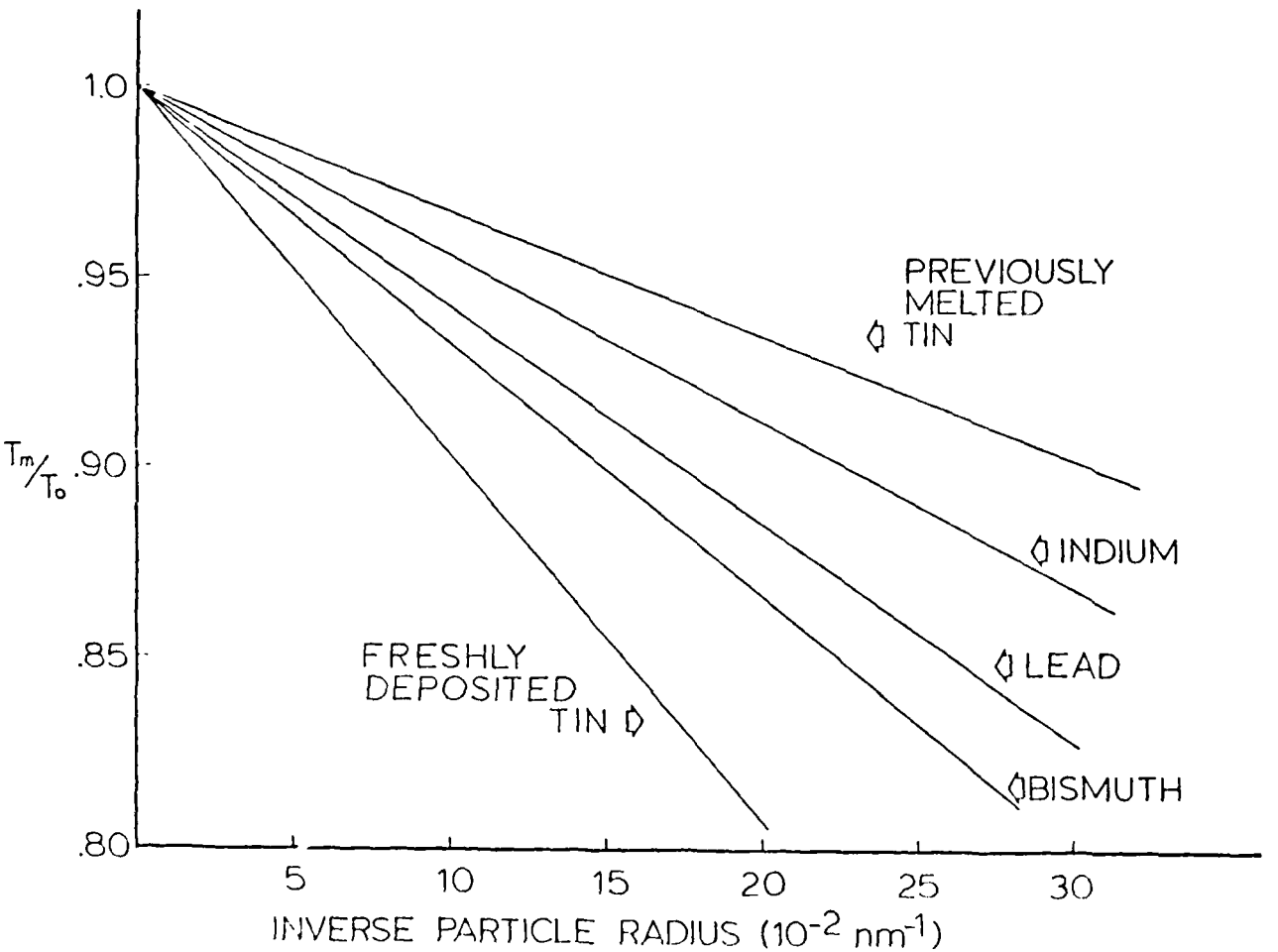


Figure 1. Graph of Reduced Melting Temperature Versus Inverse Particle Radius Showing the Least-Squares Fit of the Data for Tin, Bismuth, Indium and Lead.

same temperature. The coexistence of the metal and oxide in a single particle did not prevent the whole particle from melting at a fixed temperature.

6. In the case of lead there was found a deviation from the nearly linear relation between melting temperature and inverse radius. The small lead particles of radius below 10nm showed a steepening slope, suggesting that there is no lower limit to the melting temperature for the range of sizes studied, i.e. down to a diameter of about 10nm. The other metals were not investigated in the small size range of lead and showed no lower limit to the melting temperature.

7. Nearly continuous films were observed to thicken before melting. Isolated particles did not change their shape before melting. This result suggests that thin films should thicken and then melt at essentially the bulk melting temperature. Isolated particles of 0.1μm diameter and above melted at essentially the bulk melting temperature. The thickening phenomenon of thin films suggests that care must be exercised in using morphological information to determine whether or not the solid has melted.

8. Isolated microcrystals of tin were embedded in an amorphous carbon matrix and found to have a melting point elevation consistent with the lowering of the surface free energy of the tin and the volume expansion constraint placed on the tin particles during melting. These two effects could be separated from one another by measuring the change in slope and the change in melting temperature extrapolated to bulk sizes.

The melting temperature increase caused by the volume constraints was found to be about 10°C. This effect could also be present for the case of solid-solid transformations.

9. A simple thermodynamic model was used to account for the effect of size and the presence of a matrix on melting temperature. The model is a spherical particle surrounded by a spherical shell of matrix. The melting temperature is found by equating the free energy of the system when the particle is entirely solid to that when it is entirely liquid. The simplified result is

$$T_m/T_o = 1 - \frac{3}{rL}\left[(\sigma_s - \sigma_\ell) - \Delta E\right]$$

where

T_m = melting temperautre of the particle

T_o = bulk melting temperature

r = radius of the particle

L = latent heat per unit volume

σ_s, σ_ℓ = surface free energy per unit area for the solid and liquid respectively

$$\Delta E = \frac{6\mu\,(\delta_\ell^2 - \delta_s^2)}{2[\nu/(1+\nu) + \Gamma] + 4\mu/3\kappa}$$

with

μ = shear modulus of the shell

ν = poisson's ratio of the shell

κ = bulk modulus of the particle

δ_ℓ, δ_s = radius misfit of the liquid and solid particle respectively

$$\Gamma = \frac{2r^3 + (r+t)^3}{2[(r+t)^3 - r^3]}$$

t = shell thickness

PUBLICATIONS, REPORTS AND PAPERS PRESENTED AT SCIENTIFIC MEETINGS

1) P. R. Couchman and W. A. Jesser, "Thermodynamic Theory of Size Dependence of Melting Temperature in Metals," Nature 269, No. 5628, pp. 481-483 (1977).

2) R. A. Bayles, W. W. Gile and W. A. Jesser, "The Melting Behavior of Very Small Metal Particles," Presented to the Electrochemical Society, October 16, 1978, Pittsburgh, Pa.

3) R. A. Bayles, "Melting Behavior of Small Tin Crystallites," Ph.D. Dissertation, University of Virginia, January 15, 1979.

4) W. W. Gile and W. A. Jesser, "Study of the Melting Behavior of Small Bismuth Crystallites," Presented to the Virginia Academy of Science, May 10, 1979, Richmond, Va.

5) W. W. Gile, "Melting Behavior of Small Indium and Bismuth Particles," M.S. Thesis, University of Virginia, May 1979.

6) W. W. Gile, R. A. Bayles and W. A. Jesser, "A Comparison of the Techniques for Determining the Size Dependent Melting Temperature of Various Metals," Proceedings of the Electron Microscope Society of America, 37th Annual Meeting, Ed. G. W. Bailey, Baton Rouge, Claitor's Publishing Division, pp. 668-669 (1979).

7) G. L. Allen, W. W. Gile and W. A. Jesser, "Melting Temperature of Tin Embedded in Carbon," Presented to the Virginia Academy of Science May 1980, Charlottesville, Va.

8) G. L. Allen, W. W. Gile and W. A. Jesser, "The Melting Temperature of Microcrystals Embedded in a Matrix," Acta Met., V28, pp. 1695-1701 (1980).

9) W. A. Jesser, "The Melting Behavior of Small Particles," ARO Workshop on Powder Processing of Metals and Ceramics, Gainsville, Fla., June 1980.

10) W. W. Gile and W. A. Jesser, "Characterization of Small Pb-Bi Alloy Particles Prepared by Co-vapor Deposition," Presented to the Virginia Academy of Science, May 14, 1981 Norfolk, Va.

11) G. L. Allen and W. A. Jesser, "The Melting Behavior of Microcrystals of Lead and Aluminum," Presented to the Virginia Academy of Science, May 14, 1981, Norfolk, Va.

12) G. L. Allen, "The Melting of Small Metal Particles," M. S. Thesis, University of Virginia, May 1981.

13,14) Two papers in preparation, to be submitted in 1981.

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BIBLIOGRAPHY AND BACKGROUND LITERATURE

Experimental Literature

The first evidence for melting of small metal specimens below the bulk melting temperature was reported from electron diffraction camera data obtained from thin films.[1,2] Further electron diffraction data in support of the early work were obtained for specimens of tin[3], silver, copper, aluminum, germanium[4], gold[5,6], indium[7-9], lead[8,9], and bismuth[9]. The transmission electron microscope was directly applied to collections of crystallites by employing selected area diffraction techniques[10-14]. In addition to electron diffraction information, morphological changes have been used to detect melting[15-17]. Only one investigator has measured melting temperature of small particles individually through the application of a dark-field technique applied to lead and tin[18]. This technique, however, was not applied to in-situ deposits and hence represents data from oxidized specimens. All of the above investigations agree qualitatively with one another in showing a decrease in melting temperature with decreasing particle size; however, they differ in slope and magnitude of the T_m versus 1/r plots and are influenced to various extents by the methods employed. A comparison of the various techniques has been made[19].

Theoretical Literature

The first theoretical treatment of premature melting was a thermodynamic development in 1909 by Pawlow[20], whose work has been discussed later as a three phase equilibrium[21,22]. The next thermodynamic model was put forward by Hanszen[23] whose development was employed by others to analyze their experimental data[8,10,15,18]. A difficulty with the application of the model was a choice of the liquid

sheath thickness. It was later shown that the liquid sheath thickness was not an independent variable[22]. Melting of small particles is currently viewed as a surface driven nucleation process[22,24]. Recently a clarification of the role of surface stress in premature melting has been made by Cahn[25]. The effect of a surrounding shell on the melting temperature of small particles has also been considered[26,27].

Theoretical treatments of premature melting other than thermodynamic ones have also been presented[28-31]. These later theories are based on lattice vibration considerations of surface phonon softening on melting.

REFERENCES

1. Y. Fujiki and R. Suganuma, J. Phys. Soc. Japan 8 (1953) 427.
2. M. Takagi, J. Phys. Soc. Japan, 9 (1954) 359.
3. M. Blackman and A. Curzon Structure and Properties of Thin Films, Ed. C. Neugebauer, J. Newkirk, D. Vermilyea (Wiley and Sons, New York, 1957) 217.
4. N. Gladkich, R. Niedermayer and K. Spiegel, Phys. Stat. Sol., 15 (1966) 181.
5. P. Buffat and J. Borel, Phys. Rev. A, 13 (1976) 2287.
6. P. Buffat, Thin Solid Films, 32 (1976) 283.
7. B. Boiko, A. Pugachev, and V. Bratsykhin, Sov. Phys. Solid State, 10 (1969) 2832.
8. C. Coombes, J. Phys. F: Metal Phys. 2 (1972) 441.
9. M. Hockley, Masters of Science Thesis, University of Port Elizabeth (1976).
10. C. R. Wronski, Brit. J. Appl. Phys., 18 (1967) 1731.
11. J. Pocza, A. Barna and P. Barna, J. Vac. Sci. Tech., 6 (1969) 472.
12. M. Blackman and J. Sambles, Nature, 226 (1970) 938.

13. M. Stowell, T. Law and J. Smart, Proc. Roy. Soc., 318 (1970) 231.

14. M. Blackman, S. Peppiatt and J. Sambles, Nature, 239 (1972) 61.

15. S. Peppiatt and J. Sambles, Proc. Roy. Soc., A345 (1975) 387.

16. S. Peppiatt, Proc. Roy. Soc., A345 (1975) 401.

17. F. Jones and K. Wood, Brit. J. Appl. Phys., 15 (1964) 185.

18. R. Berman and A. Curzon, Can. J. Phys., 52 (1974) 923.

19. W. W. Gile, R. A. Bayles and W. A. Jesser, Proceedings of the 37th EMSA meeting, Ed. G. W. Bailey, Claitor's Publishing Division, (1979) 668.

20. P. Pawlow, Z. Phys. Chem., 65 (1909) 1, 545.

21. E. Rie, Z. Phys. Chem., 104 (1923) 354.

22. P. R. Couchman and W. A. Jesser, Nature, 269 (1977) 481.

23. K. Hanszen, Z. Physik, 157 (1960) 523.

24. P. R. Couchman and W. A. Jesser, Phil. Mag., 35 (1977) 787.

25. J. W. Cahn, Acta Met., 28 (1980) 1333.

26. G. L. Allen, W. W. Gile, W. A. Jesser, Acta Met., 28 (1980) 1695.

27. F. Spaepen and D. Turnbull, Scripta Met., 13 (1979) 149.

28. P. R. Couchman and C. L. Ryan, Phil. Mag., 35 (1977) 787.

29. T. Matsubara and A. Nakanishi, J. Phys. Soc. Japan 39 (1975) 1415.

30. T. Matsubara and E. Siegel, Scripta Met., 13 (1979) 913.

31. K. Hoshino and S. Shimamura, Phil. Mag. A, 40 (1979) 137.

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